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SURFACE CHEMISTRY AND REDUCTION BEHAVIOUR OF γ-ALUMINA SUPPORTED MOLYBDENUM OXIDE

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SURFACE CHEMISTRY AND REDUCTION BEHAVIOUR OF γ-ALUMINA SUPPORTED MOLYBDENUM OXIDE

by

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ABSTRACT

Alumina supported molybdenum oxide, which is usually impregnated with a promoter such as cobalt oxide, is the principal catalyst used for hydrotreating crude oil. Its unique performance may be better understood by directly measuring the surface region of the precursor oxide state prior to and following the catalyst's exposure to hydrogen gas at elevated temperatures.

An impregnated MoO_3/alumina catalyst (20 wt % MoO_3) and unsupported reference materials (Mo metal, MoO_2 and MoO_3) were examined after H_2-titration by X-ray photoelectron spectroscopy (XPS). Reduction tests and subsequent XPS analyses were conducted with the utmost care to prevent air exposure hence the uncertainty about the reoxidation of Mo species. To achieve this an elaborate reaction testing and inert transfer facility was designed and constructed.

It is concluded that: Mo on the exterior of the catalyst is not detectable in oxidation states below Mo^{4+} after hydrogen treatment (798 K, 20 h); the Mo/Al atomic ratio was unaltered after reduction suggesting sintering and/or diffusion processes are not significant; and sorbed moisture may be critical in reducing Mo^{6+} completely to the metallic state. Reduction tests performed on reference metals confirmed the integrity of the specimen transfer vessel and the transfer methodology.

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KEYWORDS: catalyst, molybdenum oxides, hydrodesulphurization, X-ray photoelectron spectroscopy (XPS), reduction.

CHIMIE DES SURFACES ET COMPORTEMENT DE RÉDUCTION DE L'OXYDE DE MOLYBDÈNE FIXÉ SUR UN SUPPORT D'ALUMINE-γ

par

J.R. Brown*

RÉSUMÉ

L'oxyde de molybdène fixé sur un support d'alumine, généralement imprégné d'un promoteur tel que l'oxyde de cobalt, est le principal catalyseur utilisé pour l'hydrotraitement du pétrole brut. On peut mieux comprendre son comportement singulier en mesurant directement la surface du précurseur à l'état oxyde avant et après l'exposition du catalyseur au gaz hydrogène à des températures élevées.

Un catalyseur de MoO_3/alumine (20 % en poids MoO_3) imprégné et des matériaux de référence non supportés (métal Mo, MoO_2 et MoO_3) ont été examinés après un titrage au H_2 au moyen de la spectroscopie photoélectronique aux rayons-X (XPS). Des essais de réduction et des analyses par XPS subséquentes ont été réalisés avec le plus grand soin afin de prévenir l'exposition à l'air et ainsi l'incertitude concernant la réoxydation des espèces de Mo. Pour parvenir à cette fin, on a conçu et construit une installation complexe d'essai de réaction et de transfert inerte.

On a tiré les conclusions suivantes : le Mo sur l'extérieur du catalyseur ne peut être détecté dans les états d'oxydation inférieurs à Mo^{4+} après un traitement à l'hydrogène (798 K, 20 h); le rapport atomique Mo/Al est demeuré le même après la réduction ce qui laisse supposer que les procédés de frittage et/ou de diffusion n'ont pas une importance considérable; l'humidité sorbée peut être critique dans la réduction complète du Mo^{6+} à l'état métallique. Les essais de réduction effectués sur les matériaux de référence ont confirmé l'intégrité du récipient de transfert des échantillons et la méthodologie de transfert.

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MOTS-CLÉS : catalyseur, oxydes de molybdène, hydrodésulfuration, spectroscopie photoélectronique aux rayons-X (XPS), réduction.

INTRODUCTION

Alumina supported molybdenum oxide, which is usually impregnated with a promoter such as cobalt oxide, is the principal catalyst used for hydrotreating crude oil fractions (1). However, the oxide form has to be considered as a precursor because under refining conditions reduction and sulphidation reactions greatly alter the chemical form of these metal species. The ease of sulphidation is critical in the activation of the catalyst as well as the physical and chemical structure of the resulting metal sulphides, i.e., the working catalyst (2).

X-ray photoelectron spectroscopy (XPS) is capable of providing semi-quantitative analysis of elements sited in the outermost region (1-3 nm) of a catalyst, determining element oxidation states and, in some cases, detecting probable compounds and degree of dispersion (3). A working catalyst's unique performance may be better understood by directly measuring the surface region of the precursor oxide state prior to and following exposure to hydrogen gas at elevated temperatures. A model of the structure of MoO_3-Al_2O_3 catalysts was developed recently based mainly on temperature programmed reduction (TPR) studies (4). This model suggests alumina supported molybdenum exists in two forms - monolayer and bilayer. Important to this model is that reduction of MoO_3/Al_2O_3 at moderate temperatures produces Mo metal in contrast to other models that predict mainly Mo^{4+}. Therefore, XPS was employed to confirm if reduction of MoO_3 (Mo^{6+}) to Mo metal occurs and in what proportions. These reduction tests and subsequent XPS analyses must be done with the utmost care to prevent air exposure hence the uncertainty about reoxidation of the Mo metal. To determine the type and concentration of Mo species on the catalyst

after reduction, an elaborate reaction testing and inert transfer facility was designed and constructed. Its usefulness in our catalysis research and development program is also reported.

EXPERIMENTAL

CATALYST PREPARATION AND INSTRUMENTATION

The catalyst, designated Mo20AlE, was prepared by pore volume impregnation of γ-alumina with a solution of ammonium heptamolybdate (4). The fresh γ-alumina had a pore volume of 0.55 cm^3 gm^{-1} and BET surface area of 190 m^2 gm^{-1}. After impregnation and drying at 393 K, the catalyst was calcined in air at 812 K for 2 h.

Catalyst particle size ranged from 180-300 μm, pore volume was 0.45 cm^3 gm^{-1} and BET surface area was 150 m^2 gm^{-1}. The Mo loading was determined to be 18.6 wt % or 4.48 atoms nm^{-2}.

The oxidic form of the catalyst was examined by XPS in three forms: as-received catalyst powder, IR-type pellet pressed from this powder, and an IR-type pressed pellet of finely crushed catalyst (<300 mesh).

The fully computerized Perkin Elmer Corporation PHI-548E XPS/AES spectrometer was equipped with an Mg anode (Mg k_α X-rays, hν = 1253.6 eV) operated at 15 kV and 20 mA. The resulting XPS spectra were collected and stored using a DEC 11/04 mini computer. Spectra have been curve-fit using an iterative non-linear least squares fitting routine available from the manufacturer. Binding energies reported are reproducible to ±0.2 eV. The base pressure of the analytical vacuum chamber is ≈10^{-10} torr. The binding energy scale of the spectrometer was calibrated using Au (Au $4f_{7/2}$ = 83.8 eV).

A low energy electron flood gun was available to compensate for specimen charging common to insulators such as catalysts. All XPS peaks were charge referenced to the Al 2p peak (74.0 eV) of the alumina support. To ensure consistency of all peak binding energies, the advantageous hydrocarbon contaminant carbon C 1s peak was also monitored. The C 1s peak energy was consistently 284.6 ± 0.2 eV referenced to the Al 2p peak at 74.0 eV. The XPS peak intensity (I) determined for a principal photoelectron line of an element (x) found in the outermost few nanometers of the catalyst can be equated to the atom fraction of that constituent (C_x) using equation 1:

$$C_x = \frac{I_x/S_x}{\sum_i I_i/S_i} \qquad (1)$$

where S_x is the empirically determined element x sensitivity factor for that photoline (5).

The Mo 3d, Al 2p, O 1s and C 1s sensitivity factors were determined as 1.74, 0.17, 0.67 and 0.25 respectively (F 1s = 1.0) using pure MoO_2, MoO_3, $CoMoO_4$, $Al_2(MoO_4)_3$, Al_2O_3, $CoAl_2O_4$, $CaCO_3$, mylar and teflon.

CATALYST DEGASSING AND HYDROGEN REDUCTION

Each 250 mg sample was degassed in a Pyrex reaction cell originally designed for BET surface area determinations. The glass cell consists of an upper manifold containing three valved inlet ports, and a lower stem of 50 mL which is connected to the manifold using a ground glass joint. The assembled cell can maintain a high vacuum of $\approx 10^{-7}$ torr. Each sample was degassed at

393 K for 16 h with constant turbomolecular pumping. Then the vacuum valve is closed and the assembly is transported under vacuum (≈2 X 10^{-7} torr) to an argon filled recirculating dry box (Ar ≥99.999%, moisture ≤0.1 ppm, O_2 <1.0 ppm). For meaningful XPS analysis the freshly degassed sample must be removed from the glass reaction cell and transferred to the spectrometer's ultra high vacuum (UHV) chamber without exposure to air (6). This transfer operation is accomplished in seven steps: (1) the sample is removed from the glass cell and deposited onto a XPS specimen holder; (2) the holder is inserted into a specially constructed UHV compatible transfer vessel capable of maintaining a vacuum of ≤10^{-8} torr; (3) the sealed vessel containing pure Ar gas at 15.5 psig is then removed from the dry box. Within minutes of removal the vessel is mounted to the introduction chamber of the XPS; (4) the vessel is opened after attaining a vacuum of ≤10^{-7} torr by pumping this chamber for 1 h using a 150 l s^{-1} turbomolecular pump; (5) the trapped Ar gas is then exhausted with the chamber re-attaining a vacuum of ≤10^{-8} torr in ≈15 min; (6) the introduction probe's fork-type gripper then clasps the sample holder and the UHV gate valve separating the introduction chamber and the analytical UHV chamber is opened; (7) the introduction probe is then inserted into the main chamber a distance central to the X-ray gun, electron gun, ion gun and electron energy analyzer. The specimen is then orientated for optimum XPS signal using the X,Y,Z translation, tilt and rotation capabilities of the introduction probe.

The introduction probe is sealed by three sets of teflon spring-mounted O-rings on either side of the introduction chamber. Differential pumping is applied between the first two sets of O-rings which are located on the atmospheric side of the introduction chamber. During transfer probe movements, the introduction and analytical chambers are ≈10^{-7} torr and ≈10^{-8} torr

respectively. A few seconds after the probe ceases movement the pressure in the analytical chamber returns to the $\approx 10^{-9}$ torr level.

The sample transfer procedure is routinely tested to ensure a sample has not been exposed to oxidizing conditions after reduction but prior to surface analysis. This test is done by reducing high purity clean Mo, Ni, etc. in flowing hydrogen gas (50 mL min^{-1}) at 773 K for 20 h and employing the identical sample transfer procedures as described above to examine the reduced metal surface by XPS.

Metal reduced in the introduction chamber of the spectrometer (H_2 - 50 mL min^{-1}, 773 K, 20 h) has been compared with specimens reduced externally and transferred via the dry box and shows no difference in the metal peak envelope, indicating the elaborate transfer facilities do prevent sample exposure to air.

RESULTS AND DISCUSSION

CATALYST STUDIES

Oxidic Catalyst

The XPS determined surface compositions of the oxidic forms of the catalyst, along with the corresponding binding energy peak positions, are reported in Table 1.

The catalyst's molybdenum surface content is ≈20% larger than the bulk value but after grinding, the difference is only ≈8% indicating a Mo enrichment at the alumina surface during impregnation. Note the surface sited contaminant hydrocarbon content is also reduced upon grinding. The Mo $3d_{5/2}$

photoline binding energy is indicative of a Mo^{6+} compound such as MoO_3 or $Al_2(MoO_4)_3$ (Fig. 1). The O 1s and Al 2p peak positions of 531.6 eV and 74.0 eV are in excellent agreement with values determined for fresh γ-alumina. The XPS measured surface oxygen content (≈61.0 At %) reasonably agrees with the value calculated using the XPS determined Mo and Al concentrations assuming the presence of only MoO_3 and Al_2O_3 species [(3.4 X 3) + (29.2 X 1.5) = 54.0 At %]. The O 1s peak has a small high binding energy shoulder at ≈533 eV indicative of structurally bound water and hydroxyl species and may explain the discrepancy (≈7 At %) between observed and calculated oxygen. No other elements were detected in the XPS analyzed volume (≈10^{16} $\mathring{A}^3$) indicating the high purity of the catalyst ingredients. The elemental detection limits for the XPS technique is ≈ 0.1 At % (≈10^{-9} gm cm^{-2}) (3,7).

Reduced Catalyst

The surface chemical results of reducing catalyst Mo20AlE are shown in Table 2. The Mo 3d photolines were computer curve fitted (Fig. 1) and indicate the degree of Mo^{6+} reduction to Mo^{5+} and Mo^{4+}. The Mo $3d_{5/2}$ peak binding energies for Mo^{6+}, Mo^{5+}, Mo^{4+} and Mo° were experimentally determined at 232.6, 231.6, 229.6 and 227.9 eV respectively (3, 8-11). The absence of a resolved Mo $3d_{5/2}$ peak at ≈228 eV is not proof that a small degree of Mo^{6+} to Mo° conversion has not occurred; XPS peak resolution limitations prevent the identification of a small amount of Mo metal sited among a large Mo^{4+} content.

Catalyst test CRT-1 in Table 2 indicates little change in the surface concentrations of Mo, O and Al compared with the oxidic form of the catalyst in Table 1. However, this ramping temperature reduction test (ramped 10 K

min^{-1} for 46 min) significantly altered the Mo chemistry with nearly half the original Mo^{6+} reduced to Mo^{5+} and Mo^{4+}. CRT-2 and CRT-3 indicate that Mo^{6+} reduction depends on temperature and time. Note the Mo^{5+} and Mo^{4+} surface sited species account for ≈70% of the Mo present after 20 h of reduction at 753 K and ≈85% after 20 h at 798°K (Fig. 1). A portion of the catalyst sample from CRT-3 was then finely crushed under Argon. XPS reveals that reduction is not uniform from the surface regions into the core of the catalyst particles (Fig. 1). After crushing, the peak attributable to Mo^{4+} decreased significantly. In both the oxidic and reduced states the crushed catalyst's Mo/Al atomic ratio is 0.10 (Tables 1 and 2). This ratio is slightly lower than the as-received catalyst's Mo/Al ratio of 0.12 (Table 1) and that determined as 0.14 after reduction (Table 2) indicating Mo is preferentially surface sited in the oxidic catalyst and reduction increases this preferential surface siting. Test CRT-4 (Table 2) was performed to determine if the method of loading catalyst into the reactor was influencing the XPS findings and if hydrogen concentration affected reduction. For example, catalyst powder within the bed of the reactor may not be in direct contact with the hot hydrogen gas stream leading to incomplete reduction. Hence, during transfer to the XPS sample probe this less reduced catalyst could mix with the highly reduced material from the upper portion of the bed resulting in underestimating the amount of Mo actually reduced.

The ratio of the reduced Mo to total Mo content ($Mo^{5+}+Mo^{4+}/Mo^{6+}+Mo^{5+}+Mo^{4+}$) measured at the surface of the pressed pellet is 0.87 (Table 2, Fig. 2b). It agrees well with that determined for the reduced catalyst powder which was 0.85 (Table 2, Fig. 1d). This is significant since it indicates that reduction tests performed on a powdered catalyst are not biased due to incomplete reduction in the reactor bed and that Mo reduction behaviour is unaffected by the use of a 5% H_2/Ar (v/v) gas stream rather than 100% H_2.

REFERENCE STUDIES

Three Mo containing compounds, MoO_3, MoO_2 and Mo metal, were examined by XPS after various treatments for calibration purposes and to determine the integrity of the transfer vessel and all accessory hardware used to prevent catalyst exposure to air and moisture prior to surface analysis.

Mo Metal

High purity Mo° was examined as received, mechanically scraped, argon ion etched, and reduced in hydrogen. The Mo oxidation states and their amounts at the surface are reported in Table 3. Prior to treatment, the Mo metal surface was largely oxidized to Mo^{6+} (MoO_3) with small amounts of Mo^{5+} and Mo° detected. Most of this oxidized overlayer was removed readily by mechanical scraping under an argon atmosphere. After a few scalpel passes, the Mo° content increased to 75% of the surface sited Mo. Argon ion sputtering (3 kV X 25 mA) of the as-received specimen for 3 min at 10^{-8} torr partially removes the oxide overlayer. No Mo^{6+} was detected with Mo^{5+} and Mo^{4+} accounting for 45% of the Mo present after etching. Another 10 min of etching (≈ 150 Å) was required to remove all Mo oxides. The ion etched Mo metal was an excellent test of the reaction vessel and all transfer hardware. The Mo 3d XPS spectrum, shown in Fig. 3 indicates only Mo° after reduction in flowing hydrogen for 5 h at 773 K. Another test using oxidized Ni metal foil and NiO powder confirmed the integrity of the reactor and transfer device. In each case only XPS peaks attributable to metal were observed.

MoO_3 and MoO_2

Unsupported MoO_3 was examined by XPS prior to and following hydrogen exposure at 773 K to determine its reduction behaviour and use as an XPS calibration material. The surface composition determined by XPS is in excellent agreement with "bulk" composition indicating the validity of the elemental sensitivity factors for Mo and O. The Mo $3d_{5/2}$ photoline at 232.6 eV is indicative of Mo^{6+} (MoO_3). The results of the reduction tests are shown in Table 4. Tests 1 and 2 indicate MoO_3, maintained at 773 K in 5% H_2/Ar (v/v) for 3 h and 25 h respectively was not reduced. After 20 h in pure hydrogen gas at 773 K however, a Mo^{4+} species is observed in the Mo 3d spectrum (Fig. 4). The third test was repeated using MoO_3 powder that was not pre-dried using the degassing procedures described previously. After only 4 h of reaction in pure hydrogen at 773 K, peaks in the Mo 3d spectrum attributable to Mo metal and Mo^{4+} oxide were measured. This interesting result indicates that moisture may play an important role in facilitating Mo oxide reduction and may explain the discrepancies reported between laboratories for MoO_3-alumina reduction behaviour. A recent paper indicates the formation of $MoO_2(OH)_2$ was important in the dispersion of Mo oxide species on alumina (12). MoO_3 reacts with water vapour according to the following equation:

$$MoO_3(s) + H_2O(g) \rightleftharpoons MoO_2(OH)_2(g) \qquad (2)$$

The oxy-hydroxide compound has appreciable vapour pressure and precipitates in a monolayer dispersion on the alumina. This species can then react with hydroxyl groups to form the MoO_4^{2-} species and eventually polyanions.

Propensity of $MoO_2(OH)_2$ or MoO_4^{2-} polyanions to react with hydrogen at 773 K may be much higher than for MoO_3 with a resulting increase in Mo^{4+} and Mo°. Note that the XPS determined Mo/O intensity ratio did not change during these MoO_3 reduction tests possibly indicating the reduced Mo species were highly dispersed on the surface of MoO_3 particles. Sintering of Mo into large particles would cause this Mo/O ratio to decrease dramatically as observed for unsupported and supported Ni oxides.

Unsupported MoO_2 was examined by XPS as received and after rinsing in 2M NaOH (13). The Mo 3d spectra in Fig. 5 indicate the surface of MoO_2 is a mixture of MoO_3, Mo_2O_5 and MoO_2 (Table 5). However, after the hydroxide rinse, the MoO_3 component was greatly reduced and Mo_2O_5 and MoO_2 became the dominant surface sited Mo species. The Mo 3d spectra of MoO_2 were very useful for verifying the computer curve fitting parameters and for defining the binding energies of peaks attributed to Mo^{6+}, Mo^{5+} and Mo^{4+}.

CONCLUSIONS

1. Molybdenum was not reduced below Mo^{4+} at the experimental conditions employed. No molybdenum metal was detected by XPS although a small Mo 3d peak at ≈228 eV could be buried under the much larger Mo^{4+} peak located at ≈229.6 eV.

2. Molybdenum, initially highly dispersed on the alumina support, could agglomerate into a few large particles or diffuse into the bulk during high temperature reduction. Therefore large errors would result in the XPS determined surface concentrations for reduced catalysts. The XPS Mo/Al atomic ratio did not change during reduction indicating sintering or diffusion of Mo are not significant.

3. Surface reoxidation or water uptake of the reduced catalysts during transfer from the reactor to the XPS was unlikely given the preventive procedures employed. The reduction tests performed on reference metals also confirmed the integrity of the transfer operation.

4. Pre-drying the catalyst overnight at 373 K and 10^{-6} torr may have been partially responsible for the lack of Mo^{6+} reduction to Mo metal; moisture may be very critical in reducing Mo^{6+} to the metallic state (12).

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FIGURE CAPTIONS

Fig. 1: XPS Mo 3d spectra of catalyst Mo20AlE powder following selected reduction tests: (1) degassed powder; (2) catalyst reduction test-1 (CRT-1); (3) CRT-2; (4) CRT-3 i; (5) CRT-3 ii.

Fig. 2: XPS Mo 3d spectra of catalyst Mo20AlE pressed pellet prior to and following reduction at 773 K for 6 h: (1) degassed and pressed oxidic catalyst; (2) CRT-4.

Fig. 3: XPS Mo 3d spectra of molybdenum metal after selected treatments: (1) as received; (2) mechanically scraped under nitrogen gas; (3) sputter etched using an argon ion gun followed by reduction in ultra high purity hydrogen for 5 h at 773 K.

Fig. 4: XPS Mo 3d spectra of MoO_3 powder: (1) degassed; (2) degassed and reduced in hydrogen at 773 K for 20 h; (3) reduced as per step 2, no degas step.

Fig. 5: XPS Mo 3d spectra of MoO_2 powder: (1) degassed; (2) degassed powder rinsed in 2M NaOH.

Table 1 - XPS analysis of oxidic MoO_3-Al_2O_3 catalyst

Surface composition [a] atomic % (±10%)	Oxidic catalyst Mo20AlE[b]				
	Bulk [c]	Powder (as received)	Powder (pressed)	Powder (ground & pressed)	E_b [d] eV (±0.15 eV)
Mo ($3d_{5/2}$)	2.8	3.4	3.6	3.1	232.6
Al (2p)	35.6	29.2	29.7	30.2	74.0
O (1s)	61.7	61.0	61.1	61.9	531.6
C (1s)		6.4	5.6	4.8	284.6
Mo/Al	0.08	0.12	0.12	0.10	-

[a] Photoelectron line for each element is shown in brackets.

[b] 250 mg of catalyst degassed under $\approx 10^{-6}$ torr vacuum for 16 h at 393 K.

[c] Assumes the bulk catalyst is 20 wt % MoO_3, 80 wt % Al_2O_3.

[d] Binding energies (E_b) are referenced to Al 2p at 74.0 eV. Values shown are averages of three determinations.

Table 2 - XPS analysis of catalyst after various reduction tests

Surface composition[a] atomic % (±10%)	Catalyst Mo20A1E reduction tests[b] (CRT)					
	CRT-1[c] (powder)	CRT-2[d] (powder)	CRT-3[e] (i) (powder)	CRT-3[e] (ii) (ground)	CRT-4[f] (pressed)	Prediction[g] (TPR model)
Mo 6+ (232.6)	1.8	1.0	0.7	0.9	0.4	2.0
5+ (231.6)	1.0 3.5	1.1 3.6	1.2 4.1	1.0 2.9	0.6 3.1	0.1 2.8
4+ (229.5)	0.7	1.5	2.3	1.0	1.8	-
0 (228.0)	-	-	-	-	0.3	0.7
Al (74.0)	25.1	27.6	30.3	29.8	31.9	35.6
O (531.0)	54.0	58.0	58.1	60.0	58.1	61.7
C (284.6)	17.4	10.8	7.5	7.3	6.9	-
Mo/Al	0.14	0.13	0.14	0.10	0.10	-

[a] Compositions are calculated from Mo 3d, Al 2p, O 1s and C 1s peak intensity and elemental sensitivity factors; Mo oxidation state percentages are estimates calculated from the curve fitted Mo 3d spectra shown in Fig. 1 and 2. Values in brackets are peak binding energy in eV units.

[b] Reductions performed in 5% H_2/Ar (v/v) flowing at 50 mL min^{-1} (except CRT-4); XPS spectra were acquired on samples transferred to the spectrometer without air exposure. Catalysts were initially degassed for 16 h at 393 K under $\approx 10^{-6}$ torr vacuum.

[c] CRT-1: reactor furnace ramped 10 K min^{-1} from 298 to 758 K

[d] CRT-2: reduction test performed at 758 K for 20 h

[e] CRT-3: (i) test performed at 798 K for 20 h
(ii) reduced catalyst from (i) above was finely ground prior to transfer from the Ar dry box to the spectrometer

[f] CRT-4: reduction test performed on the pressed pellet from Table 1 at 773 K for 20 h in static ultra-high purity hydrogen (15 psig) followed by 6 h in flowing ultra-high purity hydrogen (50 mL min^{-1})

[g] Percentage of Mo species as predicted by the two-phase Mo model of Moulijn et al., composition data are theoretical and based on the expected "bulk" values for Mo, Al and O.

Table 3 - XPS Mo 3d parameters for Mo metal prior to and following reduction

E_b(eV)[a] Mo $3d_{5/2}$ (±0.2 eV)	Mo oxidation state	% of Mo 3d envelope (±10%)[b]			
		As received[c]	Scraped[d]	Etched[e]	Reduced[f]
232.6	6+	70	10	--	--
231.5	5+	12	10	17	--
229.4	4+	--	5	28	--
228.0	0	18	75	55	100

a Experimentally determined Mo 3d peak binding energies (Fig. 3); corresponding oxidation states as determined from reference Mo compounds.

b Individual peak area percentages are determined from computer curve fitted data.

c Ultra-high purity Mo metal (5-9's), analyzed as received.

d As received Mo, mechanically scraped under nitrogen prior to XPS analysis.

e As received Mo, Argon ion etched for 3 min (3 kV X 25 mA) under ultra-high vacuum prior to XPS analysis (etch rate is ≈1.5 nm min^{-1}).

f Mo metal from d, reduced in ultra high purity, flowing hydrogen (50 mL min^{-1}) for 6 h at 773 K.

Table 4 - XPS analysis of unsupported MoO_3 prior to and following reduction

Surface composition [a] (±10%)		E_b(eV) (±0.2 eV)	MoO_3 [b]					
			Theory	As received	5% H_2 [c]		100% H_2 [d]	
					3 h	25 h	20 h	4 h [e]
Mo	1. 6+	232.6	25.0	23.0	23.6	25.0	19.4	16.5
	2. 4+	229.5	--	--	--	--	5.8	6.4
	3. 0	228.0	--	--	--	--	--	2.5
O	2-	530.8	75.0	77.0	76.4	75.0	74.8	74.6
Mo/O			0.33	0.30	0.31	0.33	0.34	0.34

[a] Determined from XPS peak intensities and instrument sensitivity factors (Fig. 4)

[b] Spec-pure MoO_3 powder, degassed under 10^{-6} torr for 16 h at 393 K.

[c] MoO_3 reduced in flowing 5% H_2/Ar (v/v) (50 mL min^{-1}) at 733 K for the two times shown.

[d] MoO_3 reduced in ultra-high purity hydrogen (50 mL min^{-1}) at 773 K for the times shown.

[e] MoO_3 was not degassed prior to the reduction step.

Table 5 - XPS analysis of unsupported MoO_2 as received and after rinse in 2M NaOH solution

E_b [a] (eV) Mo $3d_{5/2}$ (±0.2eV)	Mo oxidation state	% of Mo 3d envelope [b]	
		As received	2M NaOH rinse[c]
232.6	6+	41.0	8.0
231.4	5+	16.0	32.0
229.5	4+	43.0	60.0

[a] Peak positions (E_b) have been determined from computer curve fitted data (Fig. 5).

[b] Spec-pure grade MoO_2 powder; surface composition determination and a comparison to the expected composition was not possible due to the large presence of Mo^{6+} and Mo^{5+} oxides.

[c] MoO_2 powder was suspended in 2M NaOH solution for 1 h at 298 K, filtered and dried in air at room temperature prior to XPS.

XPS SPECTRA OF
"POWDERED" CATALYST
Mo20AlE

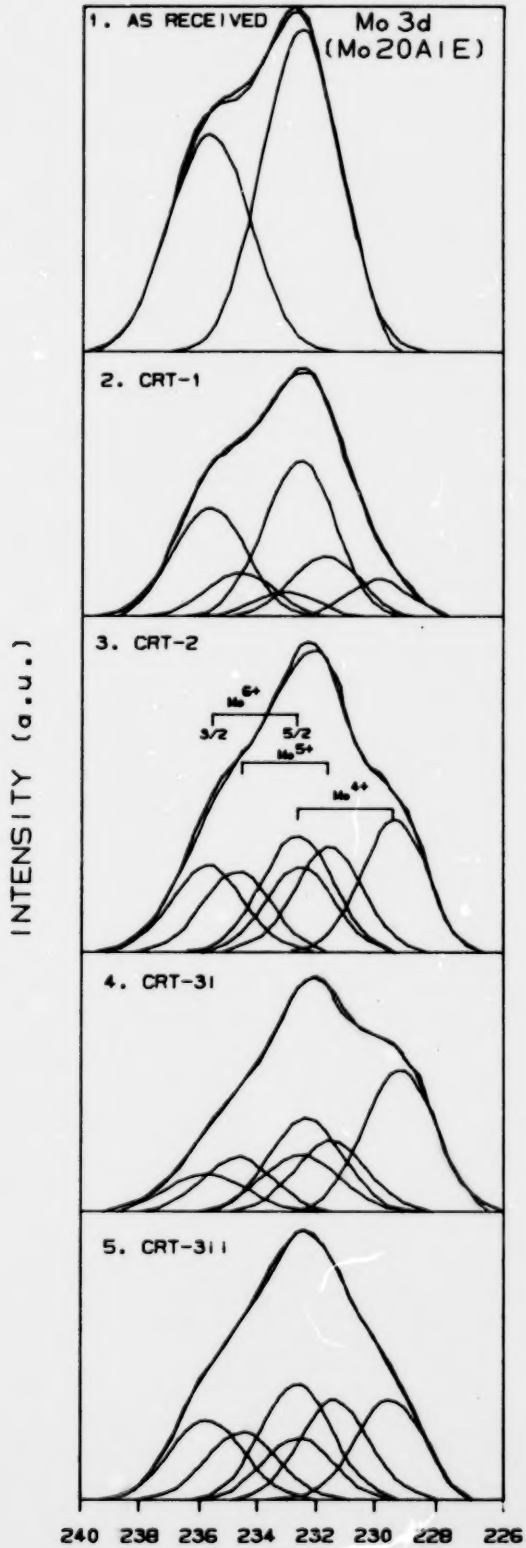

Fig. 1

XPS SPECTRA OF "PRESSED PELLET" CATALYST Mo20A1E

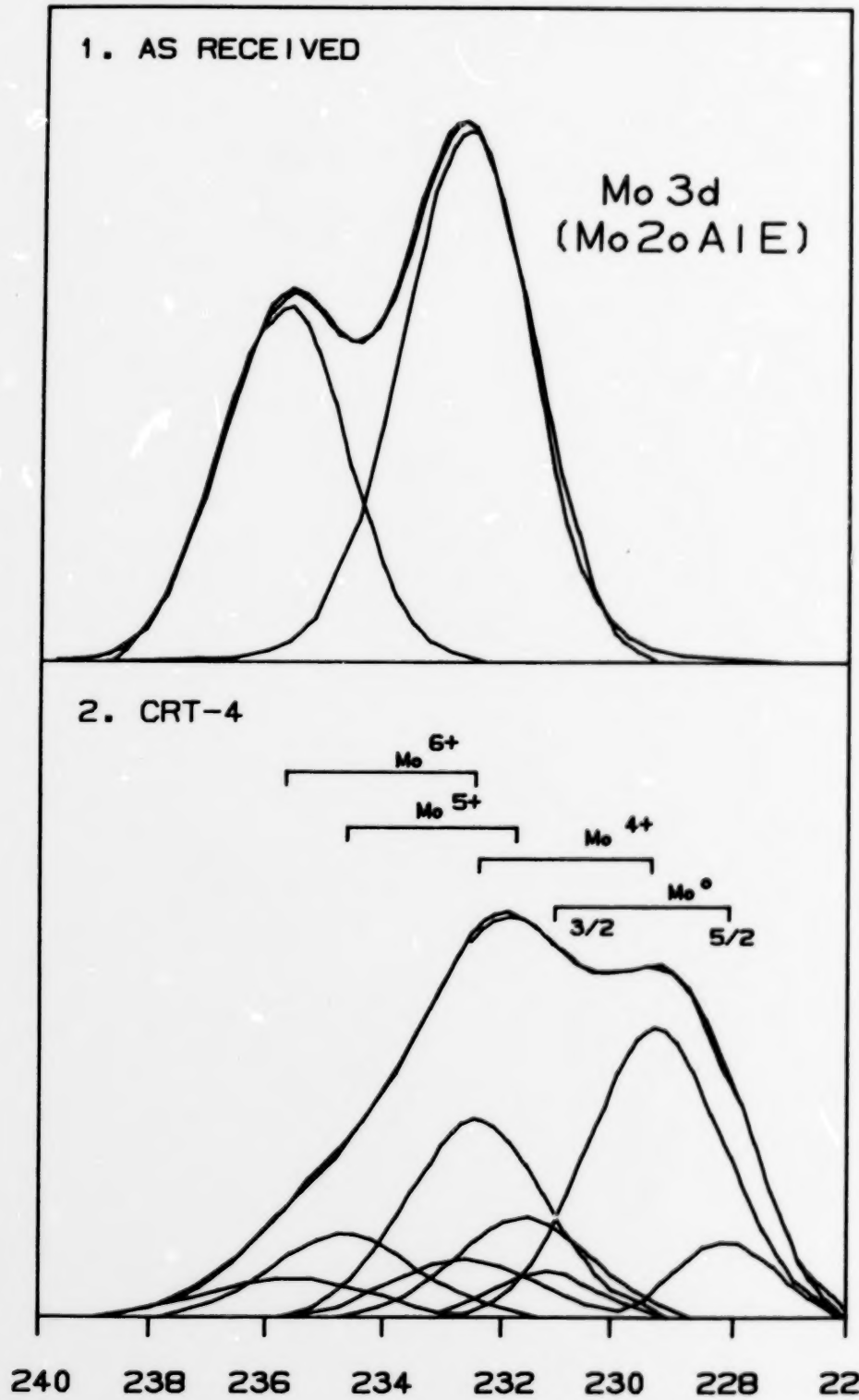

Fig. 2

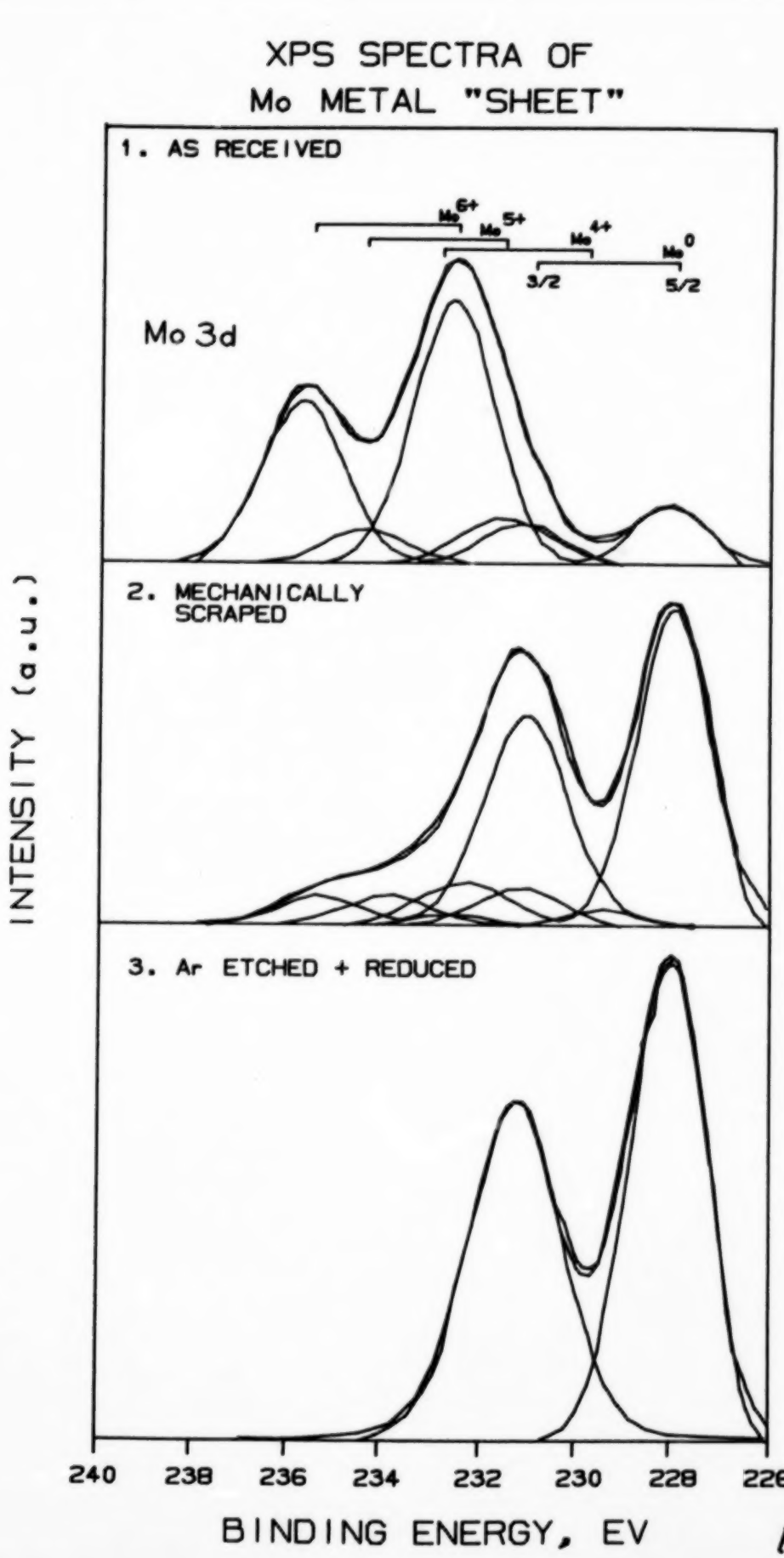
XPS SPECTRA OF
Mo METAL "SHEET"
1. AS RECEIVED
Mo 3d
Mo6+
Mo5+
Mo4+
Mo0
3/2
5/2
2. MECHANICALLY SCRAPED
3. Ar ETCHED + REDUCED
INTENSITY (a.u.)
240
238
236
234
232
230
228
226
BINDING ENERGY, EV

Fig. 3

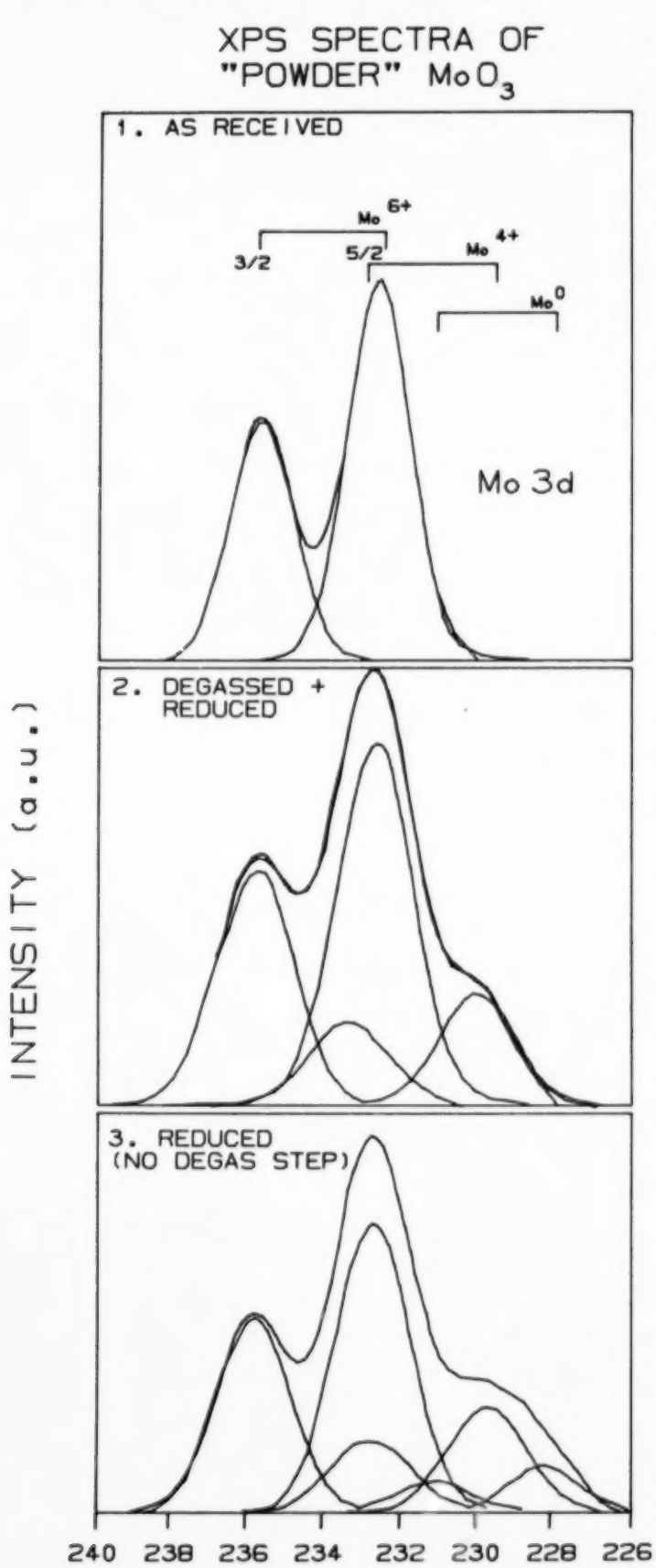
XPS SPECTRA OF
"POWDER" MoO_3
1. AS RECEIVED
Mo^{6+}
3/2
5/2
Mo^{4+}
Mo^0
Mo 3d
2. DEGASSED + REDUCED
3. REDUCED (NO DEGAS STEP)
INTENSITY (a.u.)
240 238 236 234 232 230 228 226
BINDING ENERGY, EV

Fig. 4

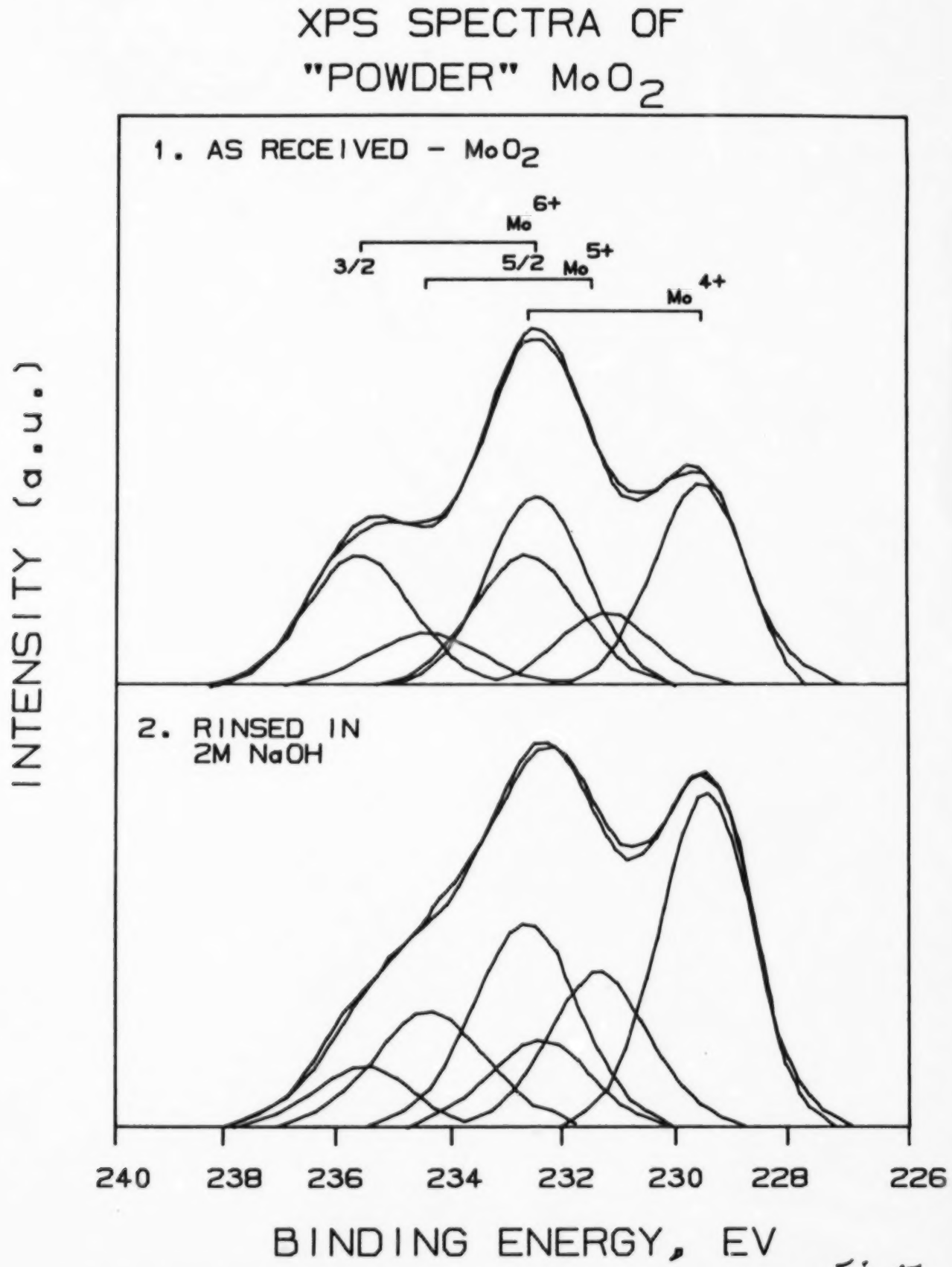
XPS SPECTRA OF
"POWDER" MoO_2
1. AS RECEIVED - MoO_2
Mo^{6+}
3/2
5/2
Mo^{5+}
Mo^{4+}
2. RINSED IN
2M NaOH
INTENSITY (a.u.)
240
238
236
234
232
230
228
226
BINDING ENERGY, EV

Fig. 5